Chapter 2

LITERATURE REVIEW

We begin this chapter with some explanation of the lithium-ion battery's chemical and physical processes. Lithium-ion battery is a rechargeable battery in which lithium-ions move from anode to cathode, and vise-versa. Physically, lithium-ion battery has three parts or three major active components. These components are anode, cathode and separator. Figure 2.1 shows the structure of a lithium-ion battery.

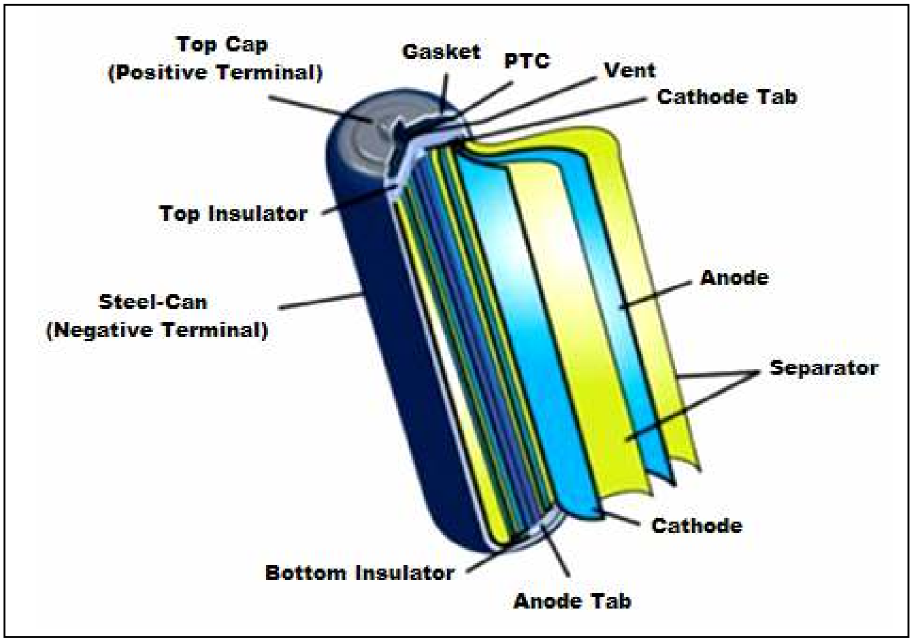
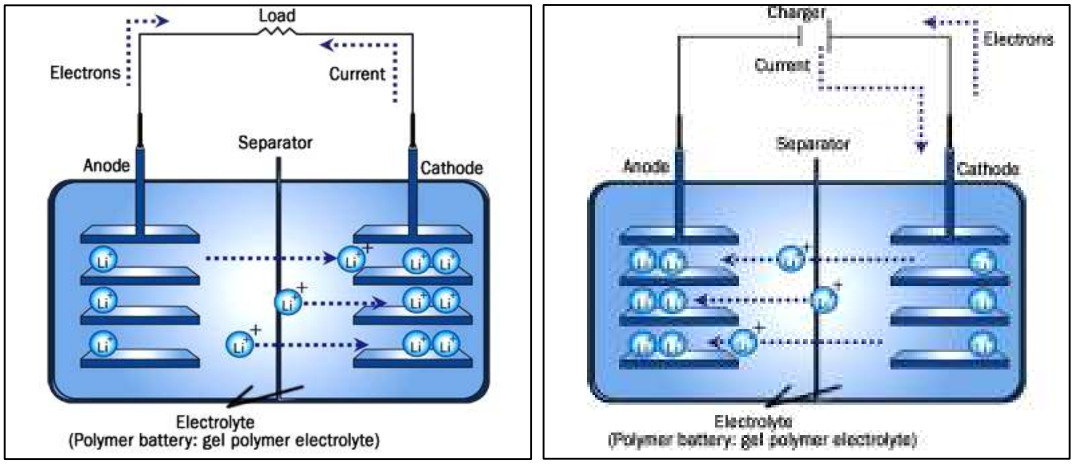


Figure 2.1: Example of the structure of Lithium-ion Battery

In rechargeable battery, the positive electrode is cathode on discharge and anode on charge. Meanwhile, the negative electrode is anode on discharge and cathode on charge. During charging, lithium-ion is extracted from cathode and inserted into anode and vise-versa during discharging. The process of lithium-ion moving into anode or cathode is referred as intercalation process while deintercalation is the process of lithium-ion moving out from anode or cathode. The mechanism of charging and discharging process are shown in the figure 2.2.



(a) **(b)**

Figure 2.2: The mechanism of (a) discharging and (b) charging process. (http://electronics.howstuffworks.com/lithium-ion-battery1.htm).

During discharging process, anode will undergo chemical reaction with electrolyte and release electrons through circuit to device and release cations (lithium-ion) to electrolyte. Lithium (Li) is easily ionized to form Li^+ plus one electron. This process is called oxidation process. Then cathode will absorb these lithium-ions and electrons that were released by anode through electrolyte and circuit. At the surface of the active material particles, lithium-ions are reduced and neutral lithium diffuses into the cathode particles. This process is called as reduction process. These two processes are commonly known as redox reaction (reduction-oxidation reaction) where anode has reduction potential and cathode has oxidation potential. Then the sum of these potential when electrons flow through an external circuit is known as voltage. These two processes can be represented in an equation called half equation. The following equations are written in units of moles, making it possible to use the coefficient *x*. The anode half reaction is

$$x\mathrm{Li}^{+} + x\mathrm{e}^{-} + 6\mathrm{C} \Leftrightarrow \mathrm{Li}_x\mathrm{C}_6$$

and the cathode half reaction (with charging being forwards) is

$$\mathrm{LiCoO_2} \Leftrightarrow \mathrm{Li}_{1-x}\mathrm{CoO_2} + x\mathrm{Li}^{+} + x\mathrm{e}^{-} \qquad \text{for} \qquad \mathrm{LiCoO_2}$$

$$\mathrm{LiMnO_4} \Leftrightarrow \mathrm{Li}_{1-x}\mathrm{MnO_4} + x\mathrm{Li}^{+} + x\mathrm{e}^{-} \qquad \text{for} \qquad \mathrm{LiMnO_4}$$

$$\mathrm{LiFePO_4} \Leftrightarrow \mathrm{Li}_{1-x}\mathrm{FePO_4} + x\mathrm{Li}^{+} + x\mathrm{e}^{-} \qquad \text{for} \qquad \mathrm{LiFePO_4}$$

The overall reaction is the sum of the anode reaction and cathode reaction.

During charging process, cathode will undergo chemical reaction causing cathode to release electron through circuit and release lithium-ion through electrolyte to anode. Hence, charging process is reversible of discharging process.

The anode in a conventional lithium-ion cell is made from Graphite (carbon), coke or lithium foil while cathode is made of lithium metal oxide, such as $\mathrm{LiMn_2O_4}$, $\mathrm{LiCoO_2}$ or $\mathrm{LiFePO_4}$. The electrolyte is lithium salt, such as $\mathrm{LiPF_6}$, $\mathrm{LiBF_4}$, or $\mathrm{LiClO_4}$, in an organic solvent. The electrolyte can be either solid or liquid and function as separator between anode and cathode. Many researchers have reported on various new developments of these battery's components. For example, Arora and Zhang (2004) reviewed on materials for separator, Aurbach et al. (2004) on electrolyte, (Whittingham 2004; Bazito and Torresi 2006; Fergus 2010) on materials for cathode and Yuan (2006) on materials for anode. Other reviews on materials and development of lithium-ion batteries were done in detail by Hazama et al. (1995), Scrosati (2000), Wakihara (2001), Nazri (2003) and Ritchie and Howard (2006). Table 2.1 shows the comparison between several cathode materials according to General Electronics Battery Co. (2006).

Table 2.1: Comparison between several materials of cathode.

Cathode materials	**$LiCoO_2$**	**$LiMn_2O_4$**	**$Li(NiCoMn)O_2$**	**$LiFePO_4$**
Reversible	140	100	150	145
Working voltage plateau (V)	3.7	3.8	3.6	3.2
Charge termination voltage (V)	4.25	4.35	4.3	4.2
Overcharge tolerance (V)	0.1	0.1	0.2	0.7
R.T. Cycle life (cycles)	400	300	400	1000
55^oC Cycle life (cycles)	300	100	300	800
Heat Flow by DSC (kJ/g)	650	150	600	10
Overcharge without PCB	4.9V/3C Explosion	6V/3C Firing	6V/3C Firing	25V/3C Pass
Price (US$/kg)	30	15	22	12
Battery energy density (Wh/kg)	180	100	170	130

Different combination of materials for anode, separator and cathode give different types of battery system. The choice of material used for these three major active components will determine the voltage, capacity, life and safety of a lithium-ion battery. Hence, the selection of materials for battery components is considered as an important aspect in improving the performance of battery. Table 2.2 shows several battery system together with its researcher group and year of publications (Ceder et al. 2002). Meanwhile table 2.3 gives the comparison of lithium-ion technologies that are being developed by various companies (Megahed and Ebner 1995).

Table 2.2: Partial list of macroscopic full-cell sandwich battery models, with year of publication.

Battery System	Research Group	Year of Publication
Li-water	D.N. Bennion	1976
Pb-PbO$_2$	J. Newman R.E. White D.N. Bennion J.N. Harb	1979 1987, 1993 1990 1999
LiAl-FeS$_2$	J. Newman	1981
Li-SOCl$_2$	R. Pollard R.E. White J. Weidner H. Wang	1984 1989 1999 2000
Zn-Br$_2$	R.E. White	1986, 1987
Na-S	H. Kawamoto	1987
Li-Ppy	R.E. White	1990
Na-FeCl$_2$	J. Newman	1990
Ni-Cd	R.E. White H. Wang	1991, 1995 1999
Ni-H$_2$	R.E. White	1991, 1994, 2000
Al-air	R.F. Savinell	1991
Li-TiS$_2$	R.E. White	1993
Li-polymer	J. Newman	1993
Li-I$_2$	P.M. Skarstad	1993
Zn-MnO$_2$	H.Y. Cheh	1994, 1999
Li-ion	J. Newman H. Wang	1994, 1996 2000
Ni-MH	R.E. White J. Newman H. Wang	1996 1997 1999

Table 2.3: Comparison of lithium-ion technologies being developed by various companies.

Manufacturer	Anode Material	Cathode Material	Nominal operational voltage (V)	Cell types	Cell sizes	Status
Sony	Petroleum coke	$LiCoO_2$	3.6	Cylindrical Square	14500, 20500, 18650, 16630 & 26XXX 48x40x8 mm 48x34x8 mm	Full production
Panasonic	Graphite	$LiCoO_2$	3.6	Cylindrical Square	17500 & 18650 40488	Sampling
Sanyo	Graphite	$LiCoO_2$	3.8	Cylindrical	18650	Sampling
Toshiba	Linear graphite hybrid	V_3O_3 $LiCoO_2$	3.0 3.6	Coin Cylindrical	2025 & 2430 18506, 18650 & 18835	Full production Full production
VARTA	Graphite	$LiCoO_2$	3.6	Unknown	Unknown	Pilot line
Rayovac	Petroleum coke	$LiNiO_2$	3.3	Coin Cylindrical	1225 & 2335 AA & D	Pilot line Experimental
Bellcore	Petroleum coke	$LiMn_2O_4$	3.6	Experimental cells only	42x77x6 mm	Experimental
SAFT	Petroleum coke	$LiNiO_2$	3.3	Cylindrical	D	Pilot line

A mathematical model of a rechargeable battery is a mathematical description of the intercalation process inside the battery. This mathematical description plays an important role in the design and use of batteries. Spotnitz (2005) stated that the mathematical model of battery can be used to represent the impact of batteries design towards their performance. According to Georen and Lindbergh (2001) numerical modeling of the transport in electrolytes has proven to be a versatile tool. Modeling can provide us result instantly and can be used to predict and understand behavior of batteries. Therefore, modeling helps in optimization of battery design. Most researchers (Doyle et al. 1993; Bergveld et al. 2002; Ceder et al. 2002; Subramanian et al. 2004) supported that simulation from the model that has been developed especially through mathematical equations is the best way to study and to fabricate better battery.

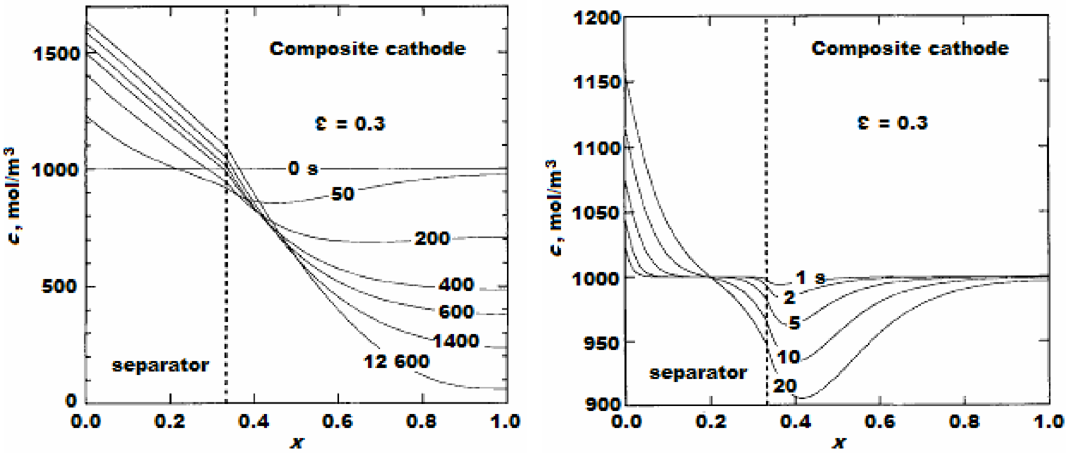
General equation that describes the behavior of porous electrode has been developed since 1962 by Newman and Tobias (1962). In their study, they have described about the theory of porous electrode and presented the derivation of the model equation that implicate concentration independent polarization equation, effect of concentration variation and deposition from a binary electrolyte. These equations are then used to determine the initial and the steady-state conditions in one-dimensional porous electrodes of uniform geometry and polarization parameters. They discovered that the types of activation polarization and mass transport of the reacting ionic species are strongly affected by the current and reaction distributions in the depth of the electrode.

In 1979, Atlung et al. (1979) have developed analytical solutions for a battery model based on alkali metal anode//liquid organic electrolyte//solid solution cathode (Li//$LiClO_4$-PC//TiS_2) to study interaction in the battery system. Three expressions have been developed for three shapes of the lithium-ion particle (thin film, cylindrical and spherical). These particles shape and the ratio between discharge times at 100% utilization of the cathode at the given load with the time constant for diffusion through the cathode particles are used to describe the cathode performance. They also discussed the rate limitations in the cathodic process and limiting current in the electrolyte phase.

West et al. (1982) used porous electrode theory (Newman and Tiedemann 1975) to develop simplified mathematical model in order to describe the dynamics of porous insertion electrode during charge-discharge process. The coupled of transport in electrode and electrolyte phase are accounted in their model. Three geometrical models with equally sized particles uniformly distributed in the electrode for three different shapes of particles (parallel sheet, long cylinders and spheres) have been developed. In formulating their model, they presented the assumption that they intended to develop the simplified model in order to keep the computational work at reasonable level. They also analyzed the porous TiS_2 electrode in an idealized organic electrolyte using numerical method. They concluded that in the porous insertion electrode system, with conventional organic electrolyte cationic, diffusion is limited by electrolyte depletion in the pores. The performance of the electrode in their study can be optimized by choosing electrolytes with transport number as close to unity as possible for inserted ions.

Then in 1984, Atlung et al. (1984) treated the composite insertion electrode behavior using analytical approach. They used the term "composite" to distinguish these electrodes from porous electrodes with liquid electrolyte. They also discussed the theoretical basis for these electrodes. Then by using a simplified model, they derived the equations to describe the distribution of potential and current during intercalation and deintercalation process. It is shown that the effective ionic and electronic conductivities, the thickness of the electrode, the volume fractions and the slope of the potential curve are dependent on the parameters that determine the discharge behavior for a given discharge current (Atlung et al. 1984).

Sony Corporation is the first company that introduced and commercialized the lithium-ion battery in 1991. This important year has sparked many researchers and battery developers to study lithium-ion battery. In 1993, Doyle et al. (1993) presented the simulation of a lithium anode//solid polymer separator//insertion cathode cell ($Li//PEO_8$-$LiCF_3SO_3//TiS_2$). They presented the derivation for this model galvanostatic charge and discharge behavior of the cell that they used based on concentrated solution theory (Newman 1991). Then the concentration profile and discharge curve were analyzed in order to determine the behavior of the cell during discharge. From this analysis, they concluded on the various methods to optimize the system parameters involving the limitations of the systems. The simulations of the concentration profile from their paper are shown in figure 2.3.



(a) (b)

Figure 2.3: Concentration Profile at (a) long time and (b) short time: $I = 10\ A/m^2$ discharge. Dashed line divides the separator and composite cathode. Initial concentration is $1000\ mol/m^3$. (Doyle et al. 1993).

Fuller et al. (1994) continued Doyle et al. (1993) study, where they discussed the simulation and optimization of the dual lithium-ion insertion cell based on the LiC_6//propylene carbonate + 1M $LiClO_4$//$Li_yMn_2O_4$ cell. The objective of their study was to develop a suitable model to evaluate and to apply it to various systems consisting of two composite electrodes composed of a mixture of active insertion material, electrolyte and inert conducting material. They compared the results from their model with experimental data and suggested that in order to improve the performance for the systems at the higher discharge rates is by increasing the electrolyte concentration. The other aspect to improve the performance of the systems is to increase the initial salt concentration but this must not exceed the maximum concentration prescribed by a solubility limit. They also presented the discharge curves for various current densities and the major process limiting high rates of discharge in the system which is the increase in concentration overpotential because of depletion of the electrolyte. From their analysis of the current distribution in the systems, they showed the importance of the rate of change of the open-circuit potential of the insertion material with the state of charge. This study also includes the discussion about optimization of the systems for particular application in terms of the attainable power and energy densities. Figure 2.4 shows the concentration profiles across the cell during galvanostatic discharge at I = 4 mA/cm^2 according to the work by Fuller et al. (1994).

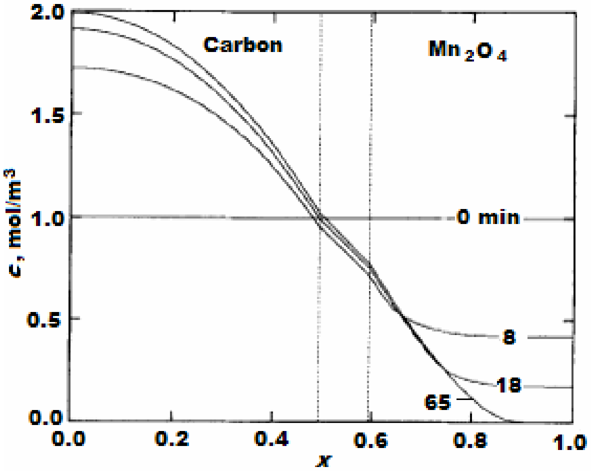
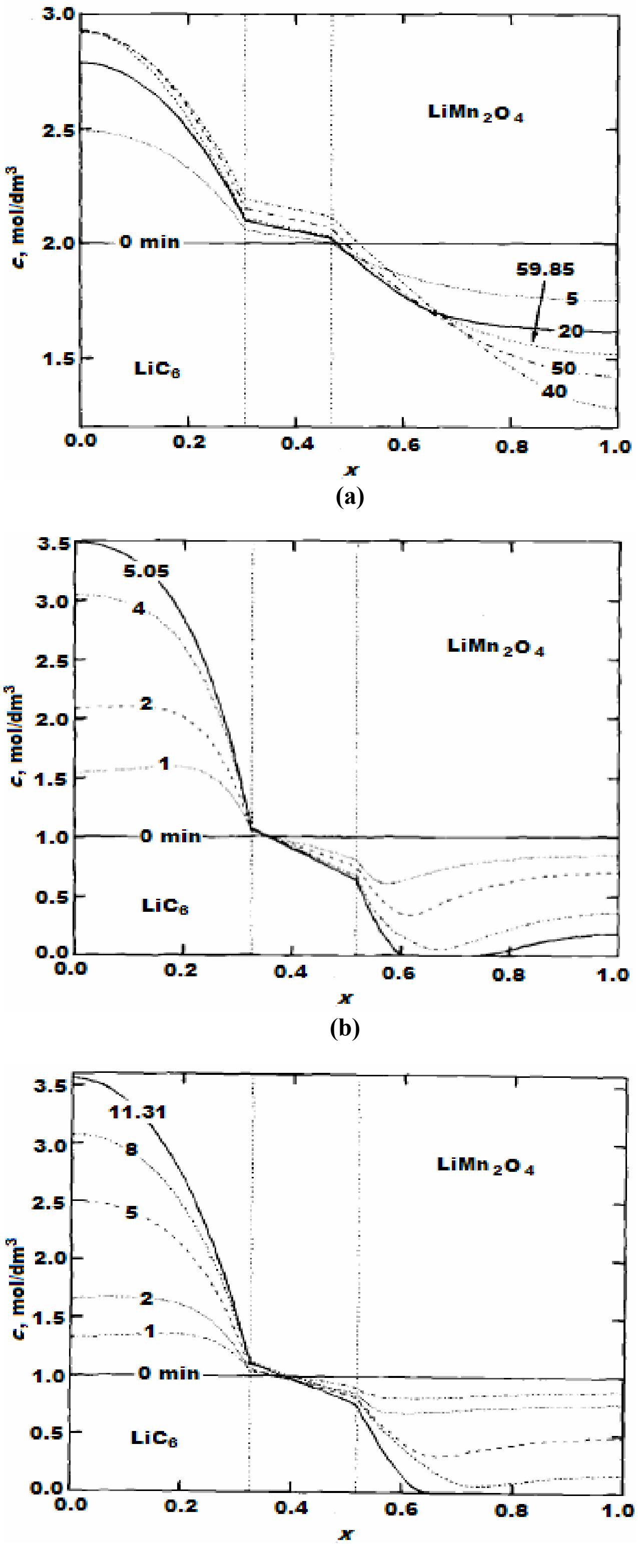


Figure 2.4: Concentration profiles across the cell during galvanostatic discharge at I = 4 mA/cm^2. Carbon negative electrode is 21.5% thicker than the manganese dioxide positive electrode. The separator region is set off by the dashed lines. (Fuller et al. 1994).

In 1995, Doyle and Newman (1995(a)) presented the use of mathematical modeling and computer simulations in understanding lithium//polymer battery performance. In their study, they reviewed a general model of this system, the categorized parameters required for the model, the role of mathematical modeling in the design process and the general approach to identify optimum values of system parameters such as electrode thicknesses and porosities.

In the same year, Doyle and Newman (1995(b)) developed a model based on Li//polymer//$LiMn_2O_4$ ohmically-dominated battery model to show the performance of rechargeable lithium based cells. With this assumption of ohmically-dominated battery model, the governing equation can be simplified and analytical expressions (cell potential, specific energy and average power in terms of the relevant system parameters) were presented. These theoretical results are very useful for design and optimization purposes. They also discovered that the open-circuit potential of the electrode reactions depends linearly on the charge of the electrode but independent of the cell potential.

Continuing their study, Doyle and Newman (1996) made comparison between experiment data and modeling results based on Li_xC_6//$Li_yMn_2O_4$ cell with different configurations for charge and discharge process by using computer simulations. These simulations were compared to experimental data for cell having different electrolyte decomposition and various electrode thicknesses. From this comparison, they obtained a good relation between the theory and the experiment data when the electrode film resistance, the effective ionic conductivity in the carbon electrodes and lithium diffusion coefficient in the carbon electrode are used as adjustable parameters. They found that the system is dominated by ohmic drop in the solution phase. In addition, with less porosity and thicker electrodes, the specific energies become larger. Figure 2.5 shows the salt concentration profiles across two different cells (Cell 1 using 2 M $LiPF_6$ in a 1:2 ratio mixture of EC/DMC with thickness of Li_xC_6 = 100μm and thickness of $Li_yMn_2C_4$ = 174μm; Cell 2 using 1 M $LiPF_6$ in a 2:1 ratio of EC/DMC with thickness of Li_xC_6 = 128μm and thickness of $Li_yMn_2C_4$ = 190μm) with certain galvanostatic discharge rate according to Doyle and Newman (1996) study.



(a)

(b)

(c)

Figure 2.5: Salt concentration profiles across (a) cell 1 during galvanostatic discharge at I = 1.75 mA/cm^2, (b) cell 2 during galvonostatic discharge at I = 10.416 mA/cm^2 and (c) cell 2 during galvonostatic discharge at I = 6.25 mA/cm^2 The separator region is set off by dashed lines. Time since the beginning of discharge is given in minutes. (Doyle and Newman 1996).

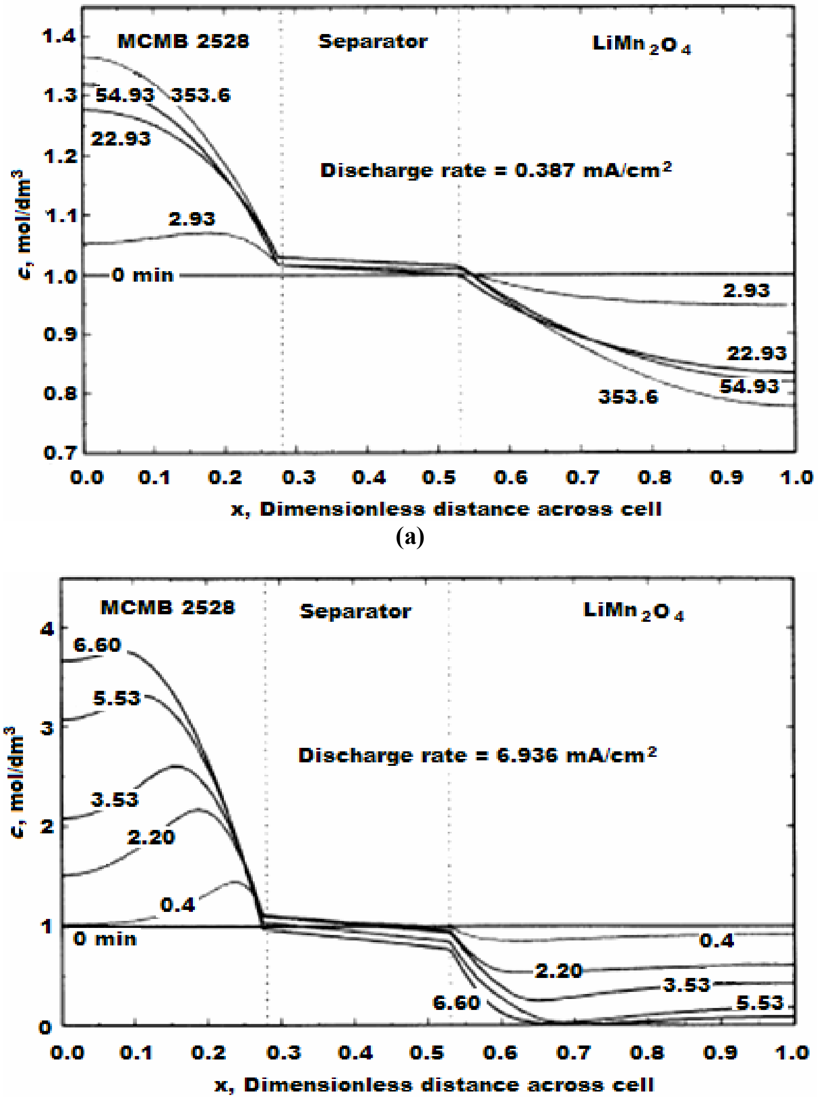
A year later Doyle and Newman (1997) considered three major cases namely solution-phase diffusion limitations, solid-phase diffusion limitations and ohmically-dominated reaction zone in developing their mathematical models. They presented the derivation of governing equations for each case and its comparison. The solution-phase diffusion limitations are a condition when they neglected the kinetic and solid-phase diffusion-limitations. In this study, they also assumed that the transport properties are independent of salt concentration. In the second case, solid-phase diffusion limitations is defined when the solution-phase concentration is uniform over the time of discharge of the battery and solid state diffusion limitations inside the insertion-electrode particles dominate a cell. This situation needs the diffusion coefficients for the lithium-ion in insertion electrode materials to be quiet low. These cases neglected the concentration gradients in the solution phase. In addition, they assumed that the charge transfer process is reversible and the reaction distribution in the porous electrode is uniform. For the third case, ohmically-dominated reaction zone, the kinetic and solution-phase diffusion limitations do not exist. Hence, before the reaction moves on through electrode, it will consume all of the available active material at that point. The effect of an open circuit potential that depends on the state of charge of the electrode, as in insertion compounds, is included in the treatment.

In 1999, Jain and Weidner (1999) did some modification towards material balance in one-dimensional mathematical models of porous electrodes. They noticed that the material balance equation is invalid because there is a nonzero volume change associated with the reaction. The modification considered two cases which is no excess electrolyte present (cross sectional area is not constant) and excess electrolyte in header (cross sectional area is constant with time). They applied the new one-dimensional mathematical model to illustrate the prediction of the delivered capacity and the electrolyte concentration in a lithium//thionyl chloride primary battery for no excess electrolyte present case, excess electrolyte in header case and for no material balance correction case.

In their later paper, Jain et al. (1999) developed and used a one-dimensional mathematical model of a spirally wound lithium//thionyl chloride primary battery for parameters' estimation and designed studies based on the fundamental conservation laws using porous electrode (Newman and Tiedemann 1975) and concentrated solution theory (Newman 1991; Newman et al. 2003; Newman and Thomas 2004). The model was used to estimate the transference number, the diffusion coefficient, and the kinetic parameters for the reactions at the anode and the cathode as a function of temperature. The model is also used to study the effect of cathode thickness on the cell capacity as a function of temperature, and it was found that the optimum thickness for the cathode-limited design is temperature and load dependent.

The world has already entered 21st century but the battery developers and researchers still continue researching on batteries due to the demand for better batteries. One of them is Botte and her group (Botte et al. 2000), who continued their research on modeling the electrochemical and thermal behavior of secondary lithium batteries. In their study, they not only considered electrochemical representation (transport phenomena and thermodynamics of the system), but also the mathematical techniques (Finite Difference Method, Finite Element Method and Control Volume Formulation), governing equation for porous electrode and mathematical software that have been used for solving the equations.

In the same year, Arora et al. (2000) published computer simulation results using experimental data from Bellcore PLION cells using the graphite//1 M $LiPF_6$ in EC:DMC (2:1)//$LiMn_2O_4$ system. The main objective of their study was to model and compare the computer simulation results with experiment data for Bellcore PLION cells. This Bellcore PLION cells was setup having higher active material loadings and competitive energy densities and specific energies to liquid lithium-ion batteries. In order to understand the transport processes in the plasticized polymer electrolyte system, they examined the cells with different electrode thickness, initial salt concentrations and higher active material loadings using mathematical model. By using the contact resistance at the current collector electrode interface as an adjustable parameter for different cells, they managed to obtain agreement between the simulations and experimental data. They also stated that the other aspect to obtain better agreement with the experimental data was by reducing the salt diffusion coefficient by a factor of two or more at the higher discharge rates. Based on this comparison, it can be concluded that the major limiting factor during high-rate discharges was due to the solution-phase diffusion limitations. The simulated salt concentration profile across the thin cell during galvanostatic discharge at 0.387 mA/cm^2 and 6.936 mA/cm^2 are shown in figure 2.6.

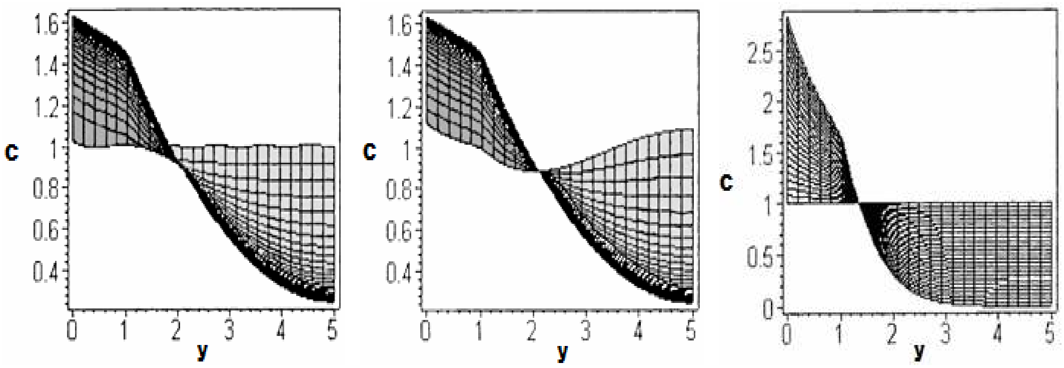


(a)

(b)

Figure 2.6: Simulated salt concentration profiles across the thin cell during galvanostatic discharge at the (a) *C/6* rate *(0.387 mA/cm^2)* and (b) *3C* rate (6.936 mA/cm^2). The separator region is set off by dashed lines. Times since the beginning of discharge are given in minutes. (Arora et al. 2000).

In 2001, Subramanian and White (2001) extended the separation of variable method to solve the governing equations of concentration distributions in solid electrodes operating under galvanostatic boundary conditions. They used this new extension method to illustrate model equations for thin film electrode, a spherical electrode particle, composite electrodes and composite spherical electrode. They also used this method to solve lithium//polymer cell model for solution phase limitations in lithium-ion cell that have been presented earlier by Doyle and Newman (1997). According to them, for boundary value problem that included the flux boundary conditions, the separation of variables is the most suitable method to use in solving these type of problem. The comparison dimensionless transient profile in a time for a lithium-ion cell sandwich with previous Doyle and Newman (1997) study and concentration profiles in a lithium-ion cell sandwich as a function on several applied current at particular time is shown in figure 2.7.



(a) (b) (c)

Figure 2.7: (a) and (b) Comparison dimensionless transient profile in a time in a lithium-ion cell sandwich with previous Doyle and Newman work. (c) Concentration profiles in a lithium-ion cell sandwich as a function on applied current *J* at particular time $\tau=1$. (Subramanian and White 2001).

From Botte et al. (2000) study, Botte and White (2001) presented the modeling of lithium intercalation in a porous carbon electrode (lithium foil//1 M $LiClO_4$-propylene carbonate//carbon fiber) by considering two cases; concentration gradient as the driving force (DFM) and chemical potential as the driving force (CPM) for diffusion. The main objective of their study was to compare these two cases performances under normal and high discharged rate conditions. The comparison was done for some limiting case and simplified model, which is for the case of potentiostatic charge and discharge of a particle carbon fiber and galvanostatic discharge of a lithium foil cell under diffusion limitations. They used the numerical technique in solving the model equations for these two cases. The comparison between CPM and DFM simulation results were presented in their paper. From their study, they found that:

- kinetic parameters obtained with the DFM may not represent the real kinetics of the system
- the DFM predicts steeper profiles for the lithium intercalation fraction inside the particle than the CPM for the simplified case of galvanostatic discharge
- the prediction for cell temperature at the given capacity using DFM is higher than CPM
- the prediction for cell discharge time at medium-high discharge rate using DFM is shorter than CPM
- DFM required less computational time than CPM in solving the model.

These results indicated that the lithium-ion interactions in the particle have a significant influence in predicting the electrochemical and thermal performance of the cell. The profile of electrolyte concentration in both cases is shown in figure 2.8.

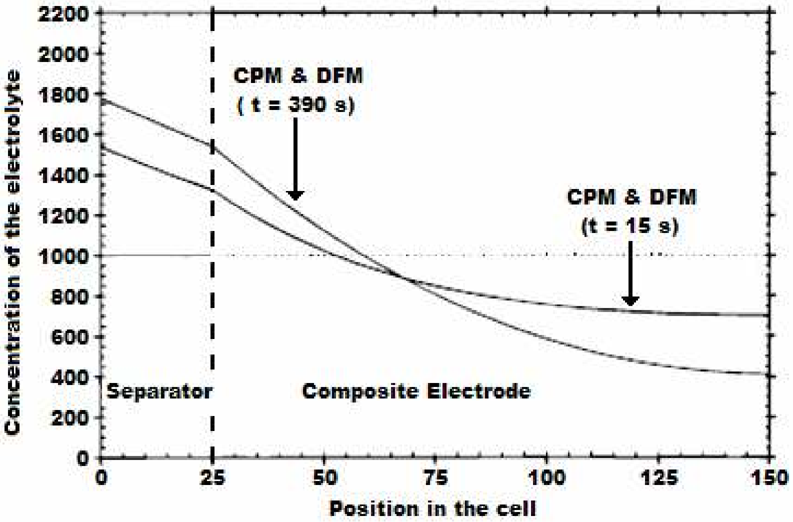


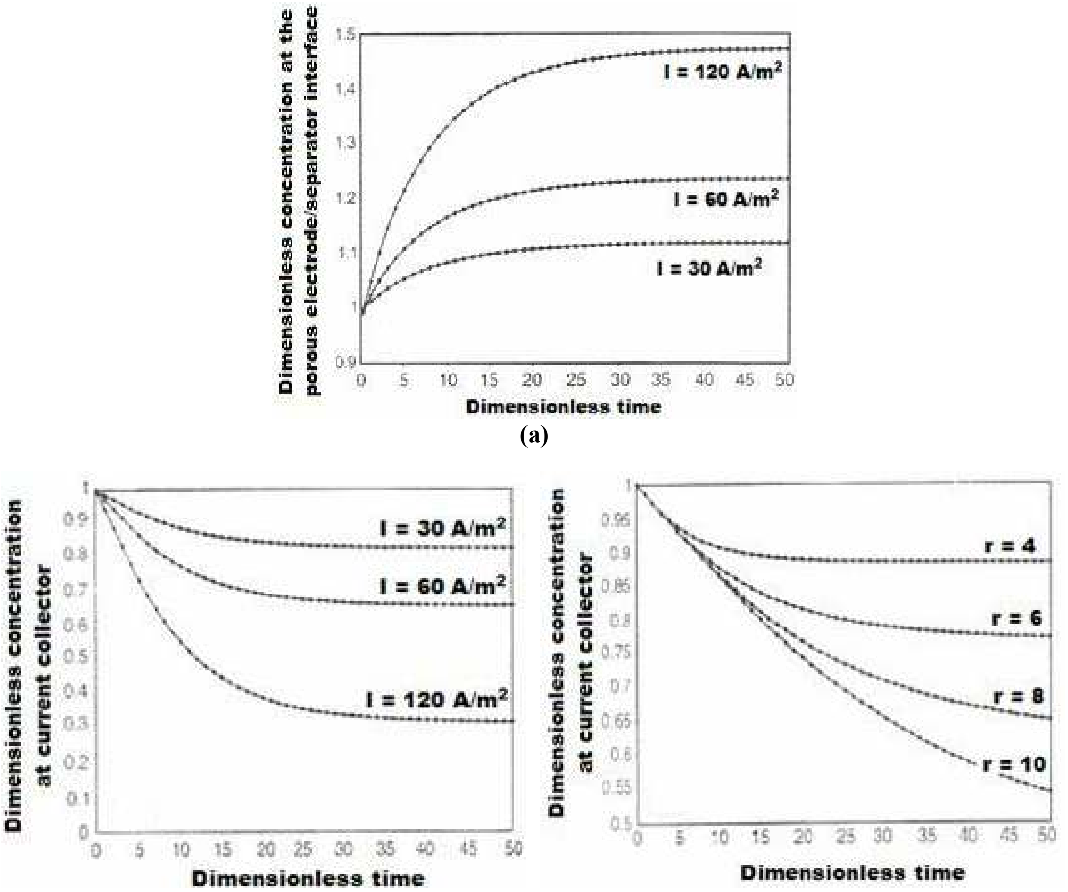
Figure 2.8: Electrolyte concentration profile for a galvanostatic theoretical discharge rate of 2C at short (*t=15s*) and long times (*t =390s*). (Botte and White 2001).

Srinivasan and Wang (2003) presented the analysis of electrochemical behavior, thermal behavior and interaction in lithium-ion cell. Specifically, they wanted to examine the level of complexity needed to adequately describe the thermal-electrochemical behavior of the cells and to gain insight into the cause for the errors seen when making approximations. They achieved this objective by performing various studies on a comprehensive two dimensional model based on a couple thermal-electrochemical approach using heat generation method. The model incorporate reversible, irreversible and ohmic heats in the matrix and solution phases and temperature dependence of the various transport, kinetic and mass-transfer parameters based on Arrhenius expressions. Furthermore, this model is used to test the hypothesis of using experimental voltage or calorimetric data to estimate the heat generation. It was shown that the use of voltage data to estimate heat generation was less rigorous compared to measuring this quantity directly from calorimetric data.

A year later, in order to understand the cause for the low power capability of the $LiFePO_4$ material, Srinivasan and Newman (2004) developed a mathematical model for lithium intercalation and phase change in an iron phosphate-based lithium-ion cell. The phase change is modeled using the shrinking core approach that envisions the existence of a core of one phase covered with a shell of the second phase with transport of lithium-ions in the shell driving the movement of the phase boundary. They discretized the model using finite differences and solved it for a constant current using the Band subroutine. They also performed the experiments to measure the equilibrium potential during lithiation in order to find the concentration ranges that defined the phase boundary. Subsequently, the understanding of the contribution for various factors that limit the performance of the electrode was carried out using galvanostatic discharged experiments. Then, they made the comparison between results from the model under constant current with experiment data. From this comparison, they found that ohmic drops in the matrix phase, contact resistances between the current collector and the porous matrix and transport limitations in the iron phosphate particle limit the power capability of the cells. Various design options, consisting of decreasing the ohmic drops, using smaller particles, substituting the liquid electrolyte with gel were explored and their relative importance was discussed. They also proposed that the model developed in their study can be used as a means of optimizing the cell design to suit any particular application.

In the same year, Devan et al. (2004) stated that the macrohomogeneous model was more useful than the cylindrical pore model. This was because the macrohomogeneous model included the possibility for current to flow in both the solid and solution phases. Consequently, the performance of a porous electrode can be predicted with the macrohomogeneous model when the conductivities of the solid phase and solution phase are comparable. Due to these reasons they presented a macrohomogeneous model for a porous electrode that includes coupled potential and concentration gradients with linear kinetics. They solved the equations to obtain an analytical expression for the impedance of a porous electrode. They also presented the effects of parameters such as exchange current density, thickness, diffusion coefficient, porosity and interfacial area on the impedance spectra. The usefulness of this analytical solution in investigating the effect of solution phase diffusion was also presented.

In Subramanian et al. (2004) work, they developed the boundary conditions for electrolyte concentration at the porous electrode//separator interface to facilitate the prediction and calculation of electrolyte concentration profile in porous electrode. The advantages of their new boundary conditions are the prediction and calculation of electrolyte concentration profile in porous electrode can be calculated directly without having to solve the concentration profile for separator. The dimensionless concentration profile that have been solved directly by them are shown in figure 2.9.



(a)

(b) (c)

Figure 2.9: Dimensionless concentration at the (a) electrode/separator interface, (b) current collector for different (b) rate of discharge and (c) values of *r* (ratio of electrode length to separator length) is plotted against dimensionless time at the *1C* rate of discharge (*60 A/m²*). The solid lines represent the exact model and the dotted lines represent the approximate solution. (Subramanian et al. 2004).

Garcı´a et al. (2005) determined the properties of rechargeable lithium-ion batteries by electrochemical and kinetic properties of their constituent materials as well as by their underlying microstructure. They developed the model framework such as kinetics equations, electrode material-electrolyte interfacial kinetics, galvanostatic discharge stresses, battery system abstraction and boundary conditions. By using microscopic information and constitutive material properties, they developed a method to calculate the response of rechargeable batteries. The method is implemented in Object Oriented Finite Element program, a public domain finite element code, so it can be applied to arbitrary two-dimensional microstructures with crystallographic anisotropy. According to them, this code has the capability of using digitized micrographs of real or computer generated microstructures to create finite element meshes by applying simple point-and-click operations. Hence, this methodology can be used as a design tool for creating improved electrode microstructures. Their results were validated against experimental Doyle (1995) result. Besides that, they explored several geometrical two-dimensional arrangements of particles of active materials to improve electrode utilization, power density, and reliability of the $Li_yC_6//Li_xMn_2O_4$ battery system. They suggested that by controlling the transport paths to the back of the positive porous electrode, maximizing the surface area for intercalating lithium ions, and carefully controlling the spatial distribution and particle size of active material the battery performance can be improved.

Valøena and Reimers (2005) measured the function of temperature and $LiPF_6$ concentration for the full set of transport properties for $LiPF_6$ in a propylene carbonate//ethylene carbonate//dimethyl//carbonate mixture. The main objective of their study was to examine the role of electrolyte properties such as lithium salt activity, lithium transference number and lithium salt diffusion coefficient. They found that the activity coefficients for $LiPF_6$ in propylene carbonate//ethylene carbonate//dimethyl//carbonate mixture was larger than one for most of the applicable concentration range, indicating solvent immobilization. For the transference number, they showed that there was little variation with concentration and temperature. Then, the diffusion coefficient was shown to have strong dependence on concentration and temperature. Furthermore, the salt activity was shown to be strongly dependent on concentration but weakly dependent on temperature at low concentration. Figure 2.10 shows the $LiPF_6$ concentration profile across the electrode.

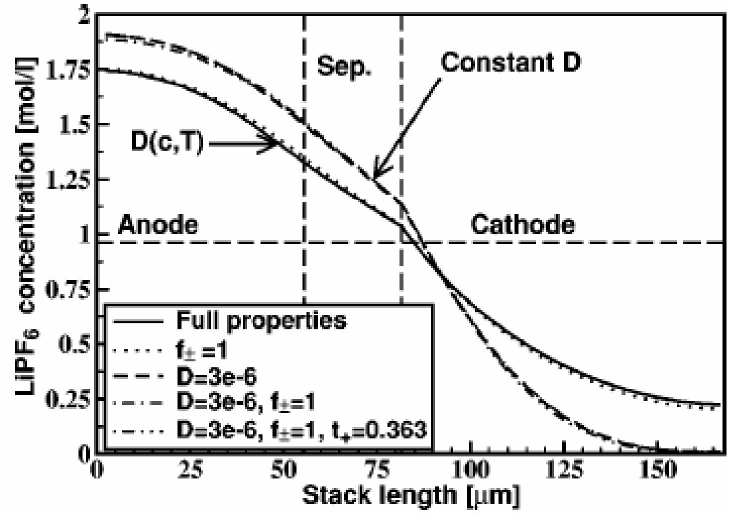
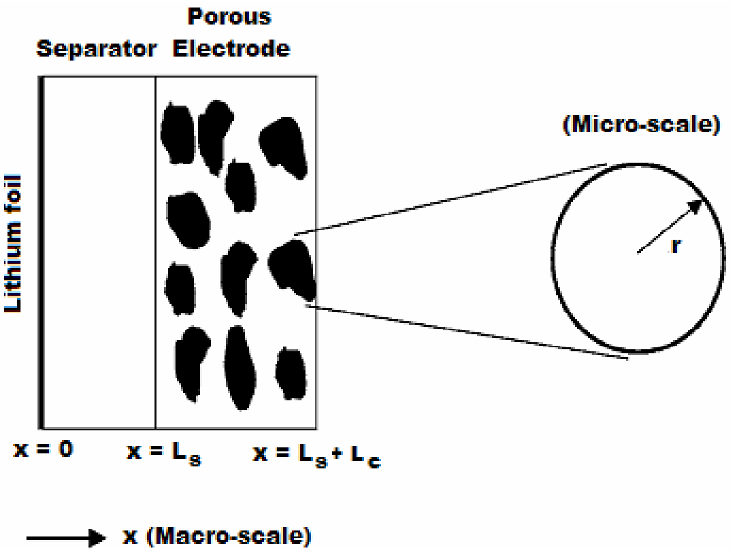


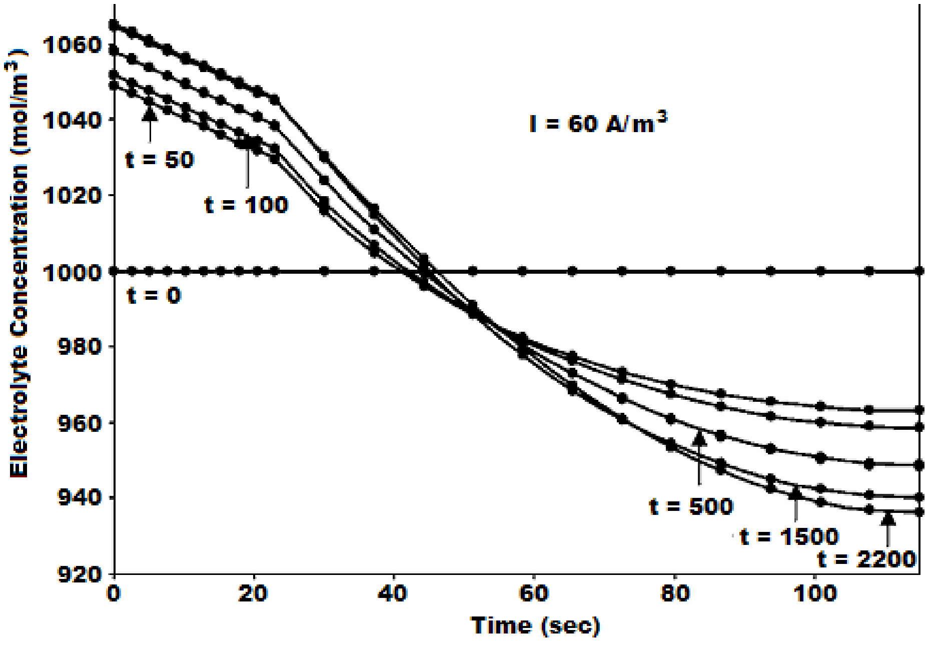
Figure 2.10: $LiPF_6$ concentration profile across the electrode after 2.0 Ah had been discharged from the cells. (Valøena and Reimers 2005).

In 2005, Subramanian et al. (2005) developed an efficient approximations for microscale diffusion inside porous electrode, which reduced the microscale diffusion from one partial differential equation to two or three differential algebraic equations. They developed it into two types of approximation models, that is for two–parameter models and higher-order polynomials profile model (three-parameter models). These approximation models are developed by assuming that the solid-state concentration inside the spherical particle can be expressed as a polynomial in the spatial direction. Then, these approximation models were used to test the exact numerical solution of particle diffusion for various defined functions (linear function, oscillatory function and exponential function) in time for the pore wall flux. Beside that, they also developed approximations for macroscale model to predict the electrochemical behavior of a lithium-ion cell sandwich. The macroscale prediction is shown in figure 2.11.

Furthermore, they also stated that the computation time for simulation could be reduced without compromising accuracy by their approximations models.



(a)



(b)

Figure 2.11: (a) Classified about micro-scale and macro-scale diffusion model and (b) Electrolyte concentration inside the cell sandwich predicted using an approximate model for the solid phase concentration is compared with electrolyte concentration obtained using 20 nodes in the particles. Solid line represents the node model (rigorous solution) and solid dots represent the approximate model. (Subramanian et al. 2005).

In 2006, in order to simulate cycling performance (800 cycles) of a lithium ion cell, Santhanagopalan et al. (2006) developed a rigorous pseudo two-dimensional (P2D) model and two simplified model that is single particle (SP) model and the porous electrode model with the polynomial approximation (PP) approach. The model developed in their work is based on LiC_6 anode//separator//$LiCoO_2$ cathode battery systems. The FOTRAN solver called as DSART was used to solve these three models (P2D, SP and PP model). They made comparison amongst these three models up to 1*C* rate of discharge. From these comparisons, they discussed the limitation and the advantage of the simplified model that have been used. They found that SP model is the best model to simulate accurately the cycling of lithium-ion battery up 1*C* rate of discharge while PP model for rates higher than 1*C*. They also presented the result of their comparison of discharge curves predicted by both model (PP model and SP model) and concentration profile for solution phase at various rates of discharge as predicted by the PP model for the full cell (LiC_6 anode//separator//$LiCoO_2$ cathode). The concentration profiles for solution phase at various rates of discharge as predicted by the PP model are shown in figure 2.12.

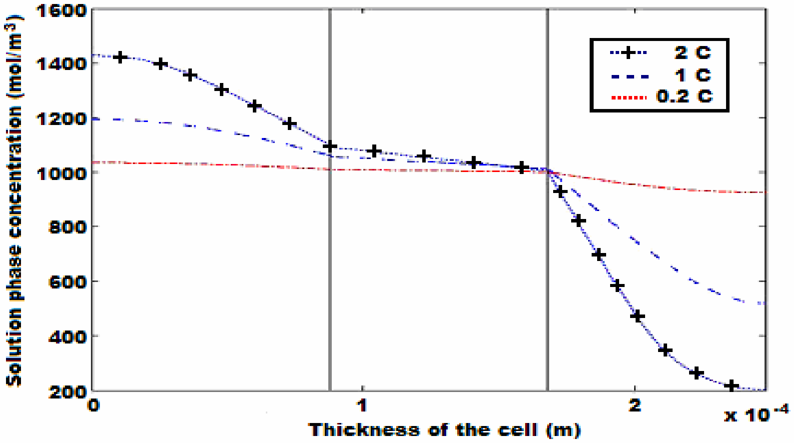


Figure 2.12: Change in the solution phase concentration at various rates of discharge as predicted by the PP model. (Santhanagopalan et al. 2006).

Then, in 2006, Ning et al. (2006) developed a generalized first principle charge and discharge model. The model is based on loss of the active lithium ions due to the electrochemical parasitic reaction and rise of the anode film resistance. The charge and discharge cycling process is simulated continuously to update parameters such as the anode film resistance and the lithium concentration in the anode at the beginning of discharge. This work included the simulation of:

- charge and discharge performance
- cycling performance
- the parasitic reaction at anode/electrolyte interface
- cycle life with multiple cycling regimes

Beside that, they also presented the comparison of simulated and experimental discharge curves at different cycles. These simulations are done for 2000 charge and discharge cycles using Compaq Visual Fotran. The effect of parameters such as depth of discharge (DOD), end of charge voltage (EOCV) and over voltage of the parasitic reaction on the cycle life behavior has been quantitatively analyzed. The discussion of model development such as schematic diagram, theories, assumptions, governing equations and boundary conditions were also presented in their study. Figure 2.13 shows the simulations of lithium concentration in the electrolyte phase according to Ning et al. (2006) work.

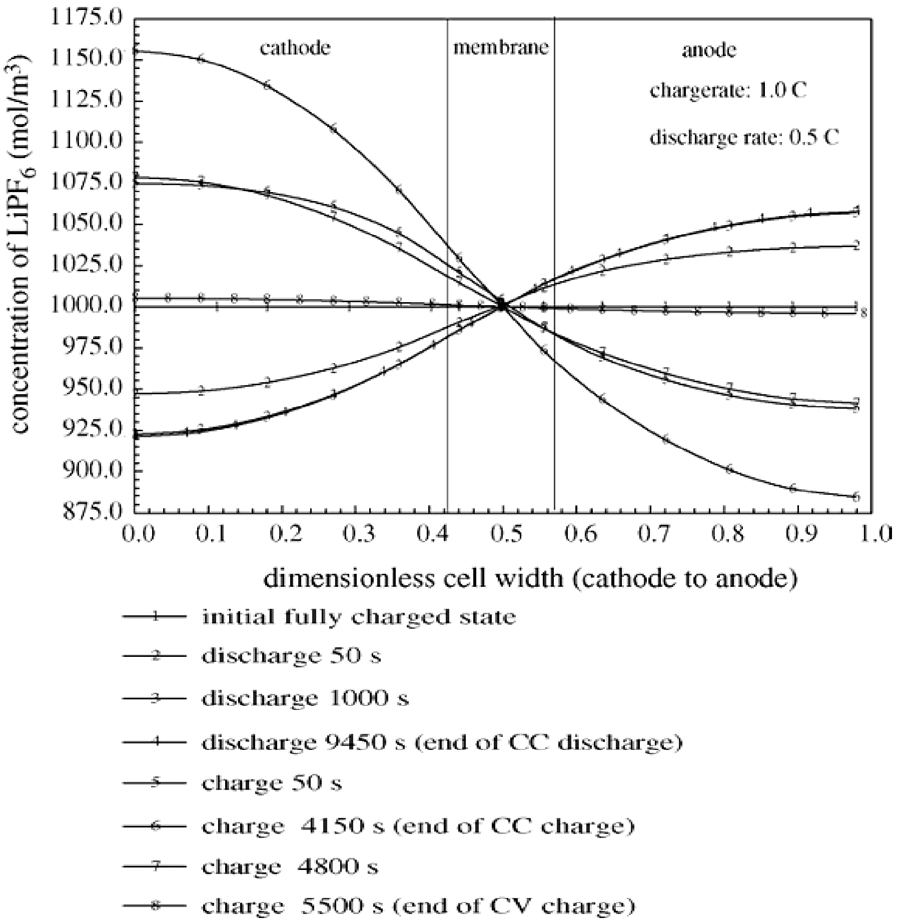
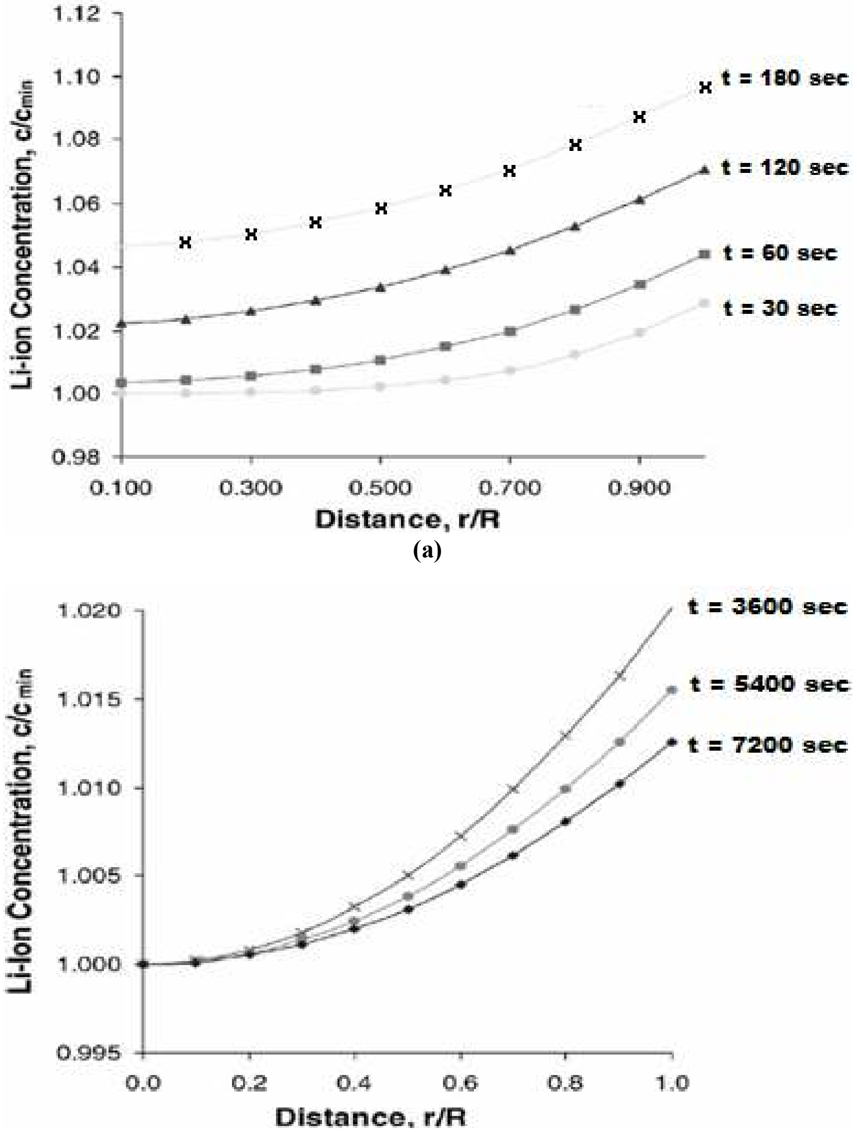


Figure 2.13: Simulations of lithium concentration in the electrolyte phase. (Ning et al. 2006).

Hashim Ali and Mohamed (2006) presented a theoretical investigation of lithium transport through a $LiMn_2O_4$ film electrode used in fabrication of a lithium-ion cell. They used the analytical approach called Laplace Transform to solve the model equation in order to predict the dynamic behavior of the electrolyte concentration within the electrode in the discharge mode. This study is a continuation of Hashim Ali and coworkers' previous study (Hashim Ali et al. 2002; Hashim Ali et al. 2003; Hashim Ali et al. 2004). In Hashim Ali et al. (2002) and Hashim Ali et al. (2004), they have considered two phases, which is solid-phase of cathode and solution-phase of cathode. These two phases have also been discussed earlier by Doyle and Newman (1997). Figure 2.14 to 2.18 show the results from their previous work.



(a)

(b)

Figure 2.14: Concentration profile in solid-phase across the cathode for (a) short-time interval and (b) long-time interval during galvanostatic discharge *I=1.39 mA/cm^2*. (Hashim Ali et al. 2002).

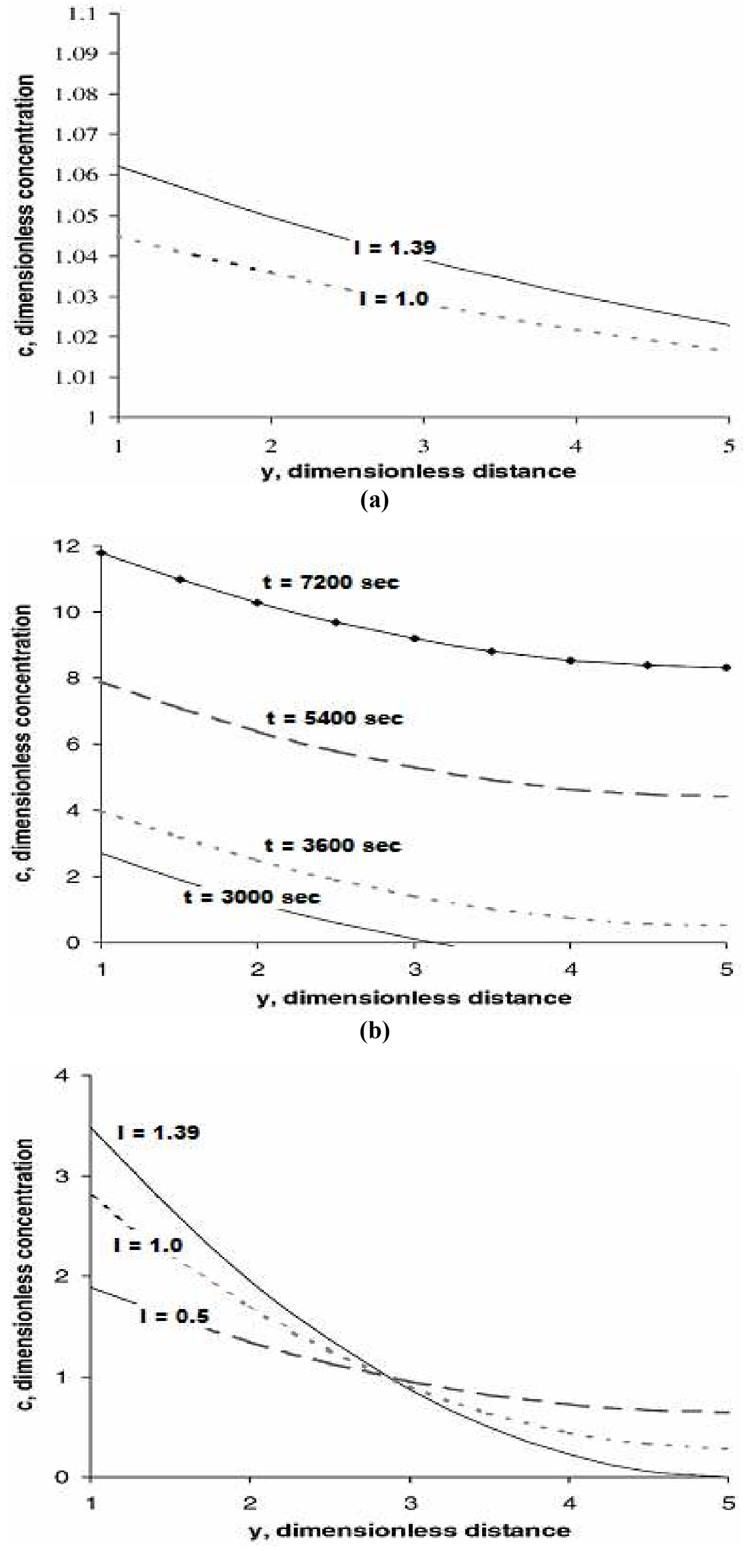
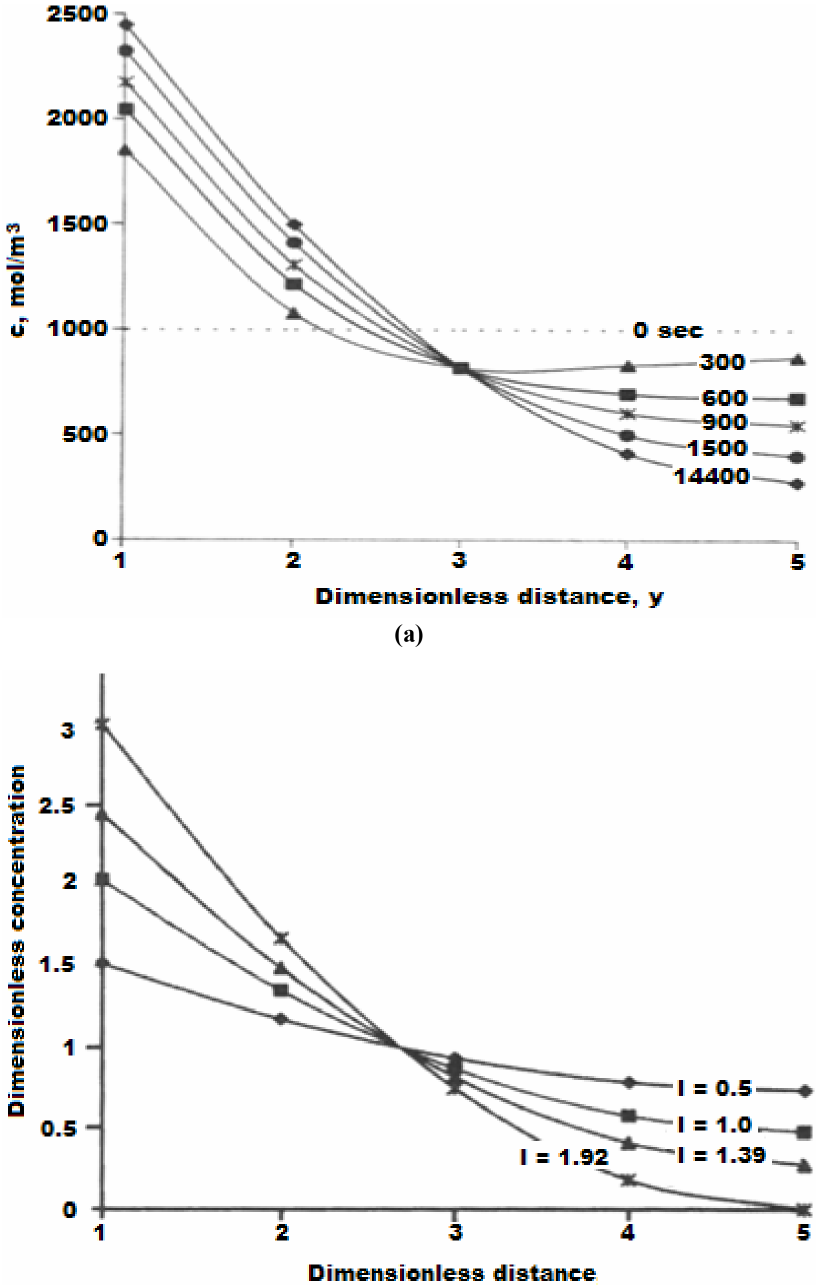


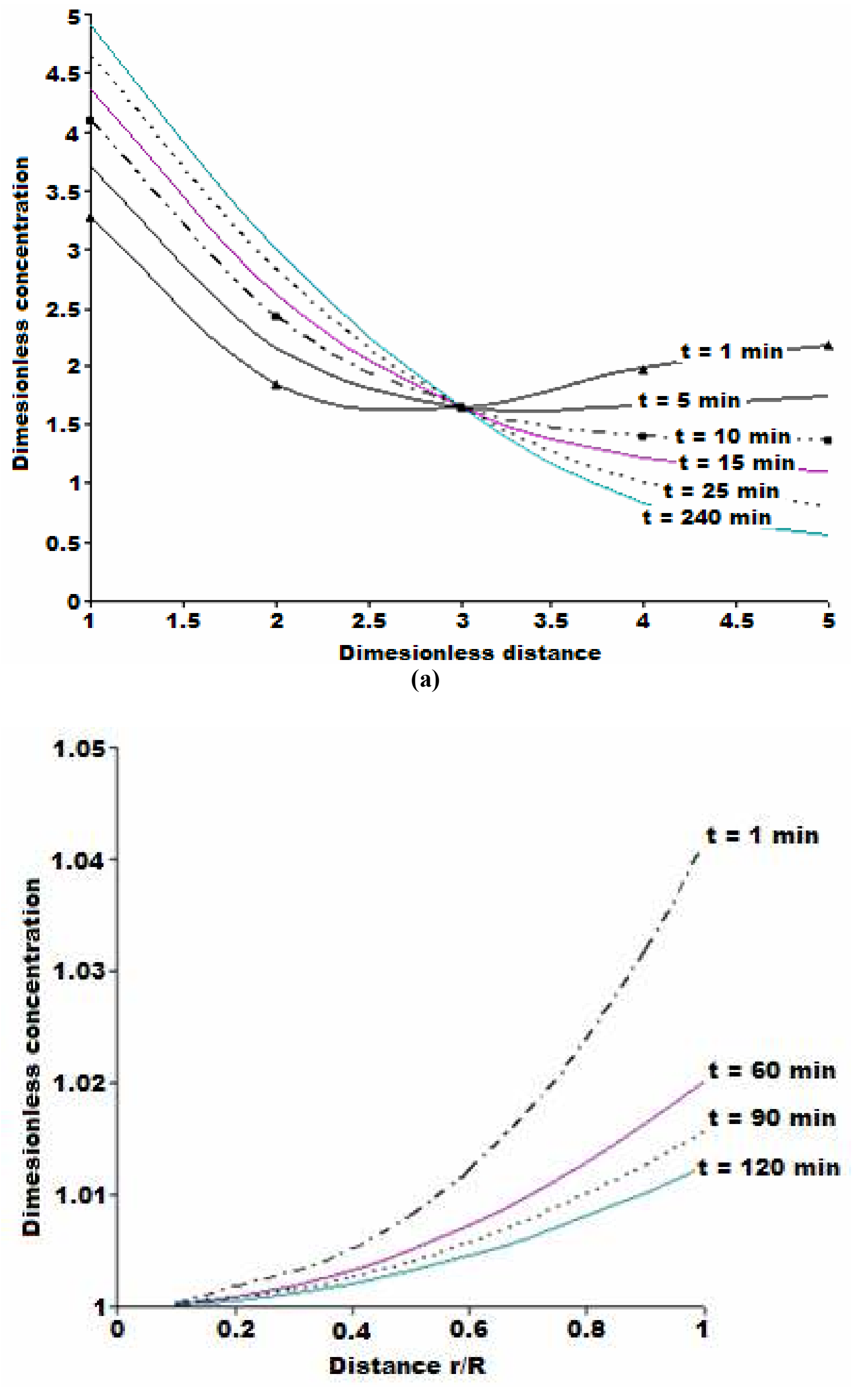
Figure 2.15: Concentration profile in solution phase across the cathode for (a) short-time interval during galvanostatic discharge (*I=1.0 mA/cm*^{2} and *I=1.39 mA/cm*^{2}), (b) long-time interval during galvanostatic discharge (*I=1.39 mA/cm*^{2}) and (c) various discharge current rate, *I*. (Hashim Ali et al. 2002).



(a)

(b)

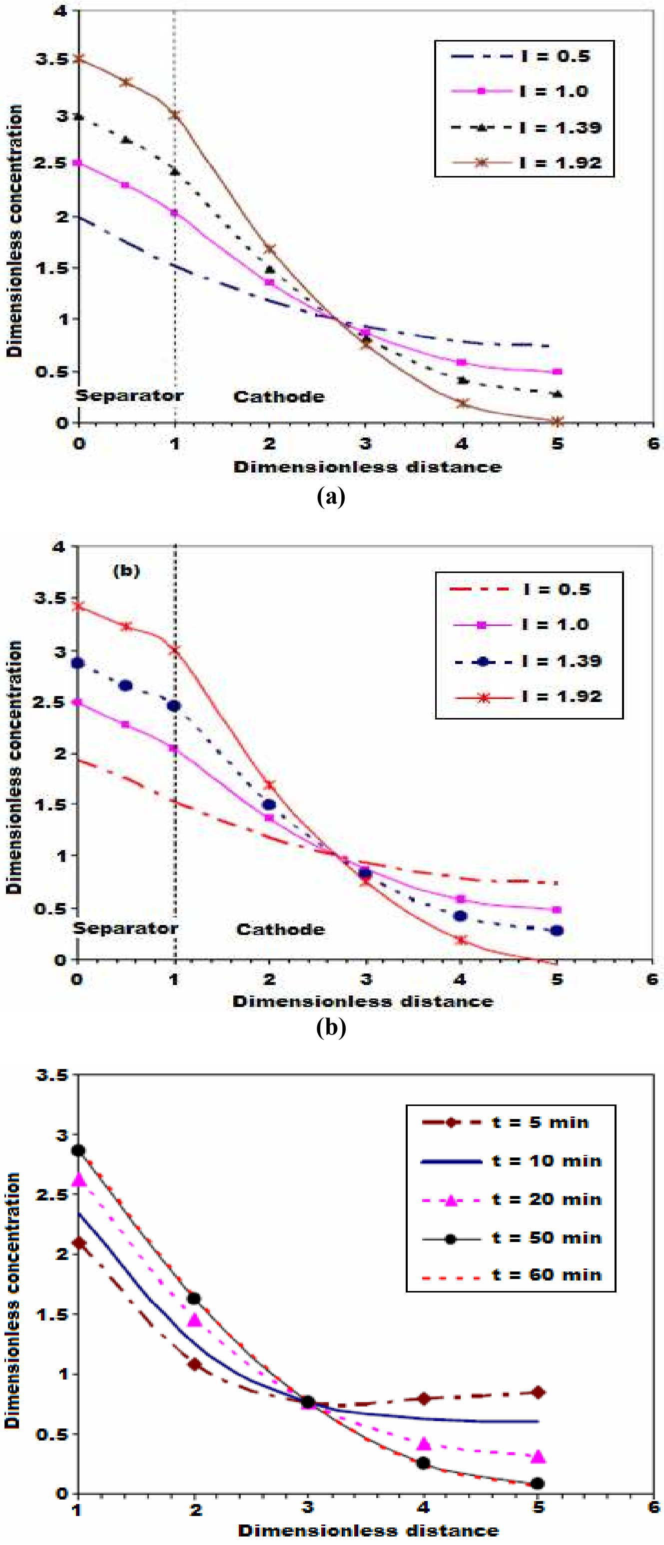
Figure 2.16: Profiles of lithium ion concentration for various (a) times (*t = 0, 300, 600, 900, 1500* and *14400* seconds) with the initial concentration 1000 mol/m^3 and (b) discharge current (*I = 0.5, 1.0, 1.39 and 1.92mA/cm^3*). (Hashim Ali et al. 2003).



(a)

(b)

Figure 2.17: Profile of lithium-ion concentration in (a) solution phase and (b) solid phase under various time, *t.* (Hashim Ali et al. 2004).



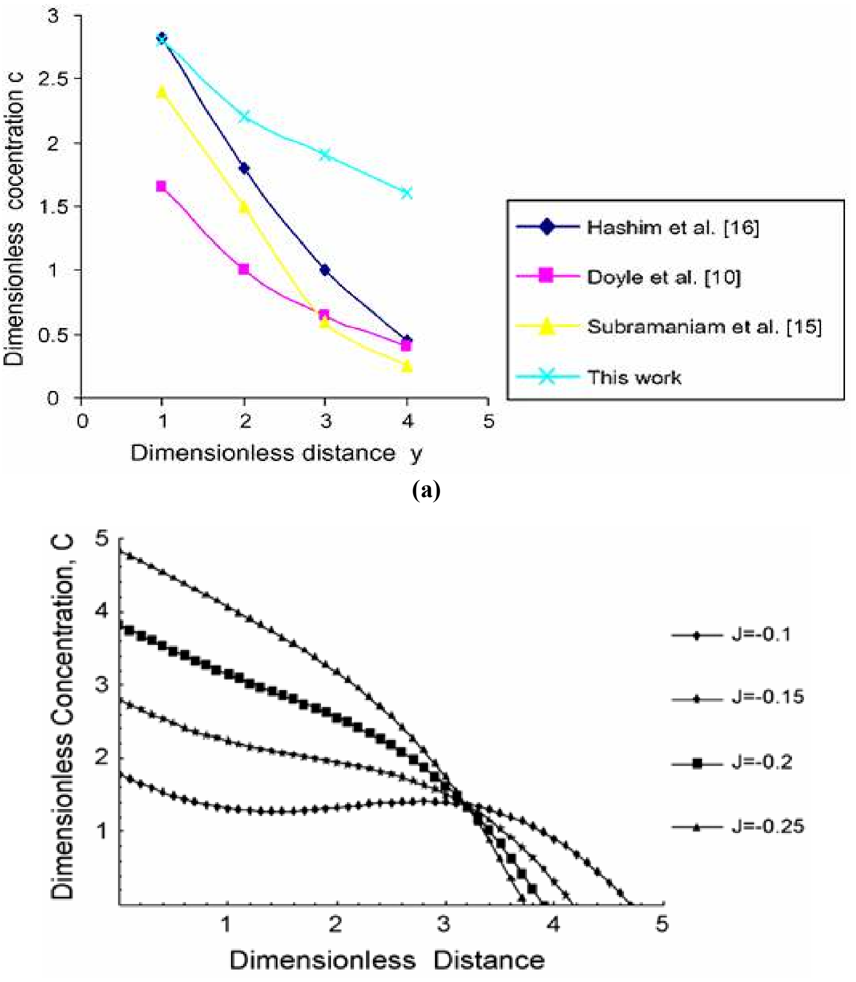
(a)

(b)

(c)

Figure 2.18: Concentration profile across (a) separator and cathode during galvanostatic discharge at *60 min* for *I = 0.5, 1.0, 1.39* and *1.92 mA/cm*^{2}, (b) separator and cathode during galvanostatic discharge at *240 min* for *I = 0.5, 1.0, 1.39* and *1.92 mA/cm*^{2} and (c) cathode during galvanostatic discharge of *I = 1.92 mA/cm*^{2} for time *t=5, 15, 20* and *60 minutes*. (Hashim Ali and Mohamed 2006).

Johan and Arof (2007) solved the non-homogeneous material balance equation for the solution phase of a lithium cell analytically using Green's function. The material balance equation used in this work was developed by Hashim Ali et al. (2002). The results of their work and comparisons with other researchers are shown in figure 2.19.



(a)

(b)

Figure 2.19: Concentration profiles in solution phase across cathode (a) compared with previous published results and (b) during galvanostatic discharge at a particular time ($\tau = 1$). (Johan and Arof 2007).

In the same year, Subramanian et al. (2007) presented the progress of effective approach that they have made in simulating lithium-ion battery models in real time for simulation and control in hybrid environment. This was done by reducing the number of differential algebraic equation (DAE) to find solutions to the battery model without losing accuracy in order to save computation time. The battery model used for this simulation is derived from the first principles as an isothermal pseudo two-dimensional model with incorporation of concentrated solution theory, porous electrode theory and variations in electronic/ionic conductivities and diffusivities using the Bruggmann coefficient. Figure 2.20 shows the flowchart of their work regarding to the model simplification. They used this approach to simulate LiC_6//separator//$LiCoO_2$ battery system. According to them, their simplified model can be used to predict intrinsic variables such as overpotential, solution-phase potential, solid-phase potential and electrolyte concentration accurately compared to the rigorous numerical model. Figure 2.21 shows the graph electrolyte concentration comparison using their simplified model with rigorous numerical model.

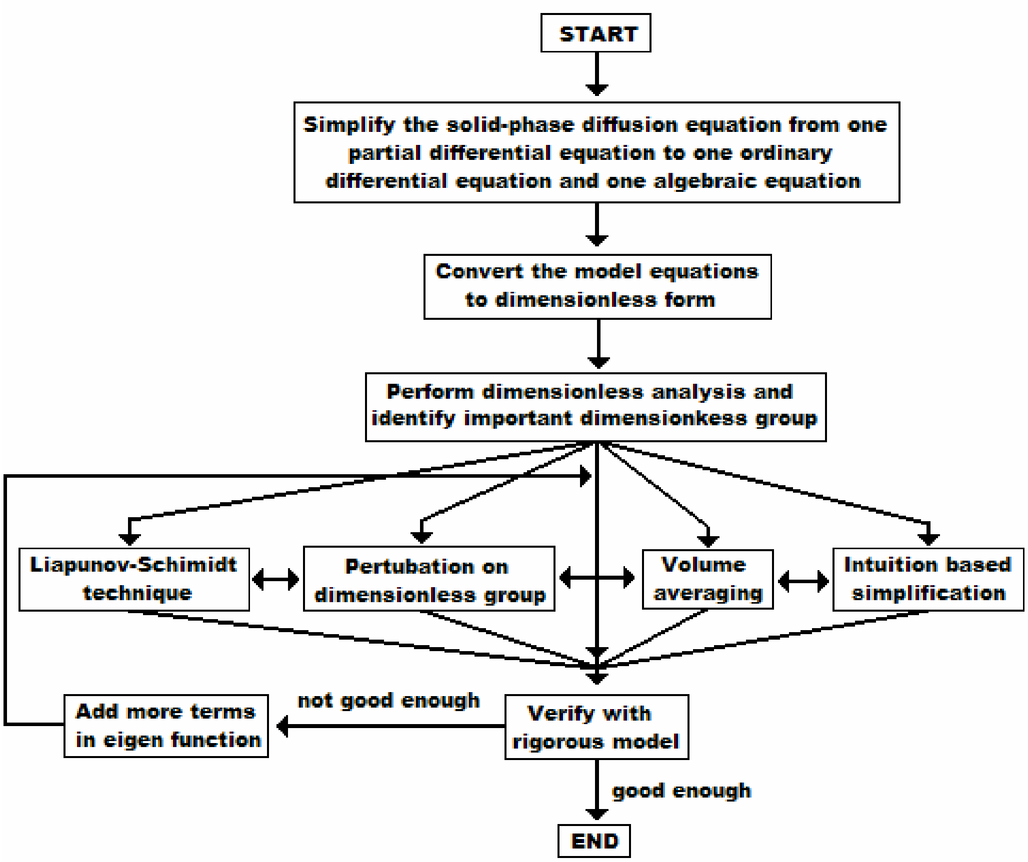


Figure 2.20: Flowchart of Subramanian et al. work regarding to their model simplification (Subramanian et al. 2007).

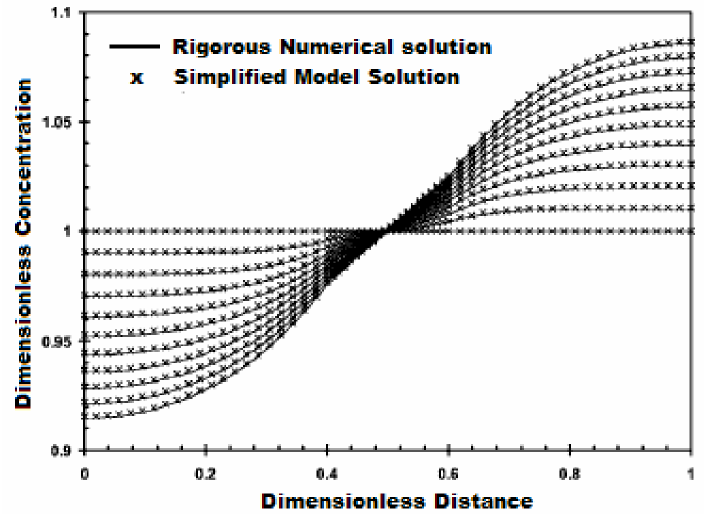
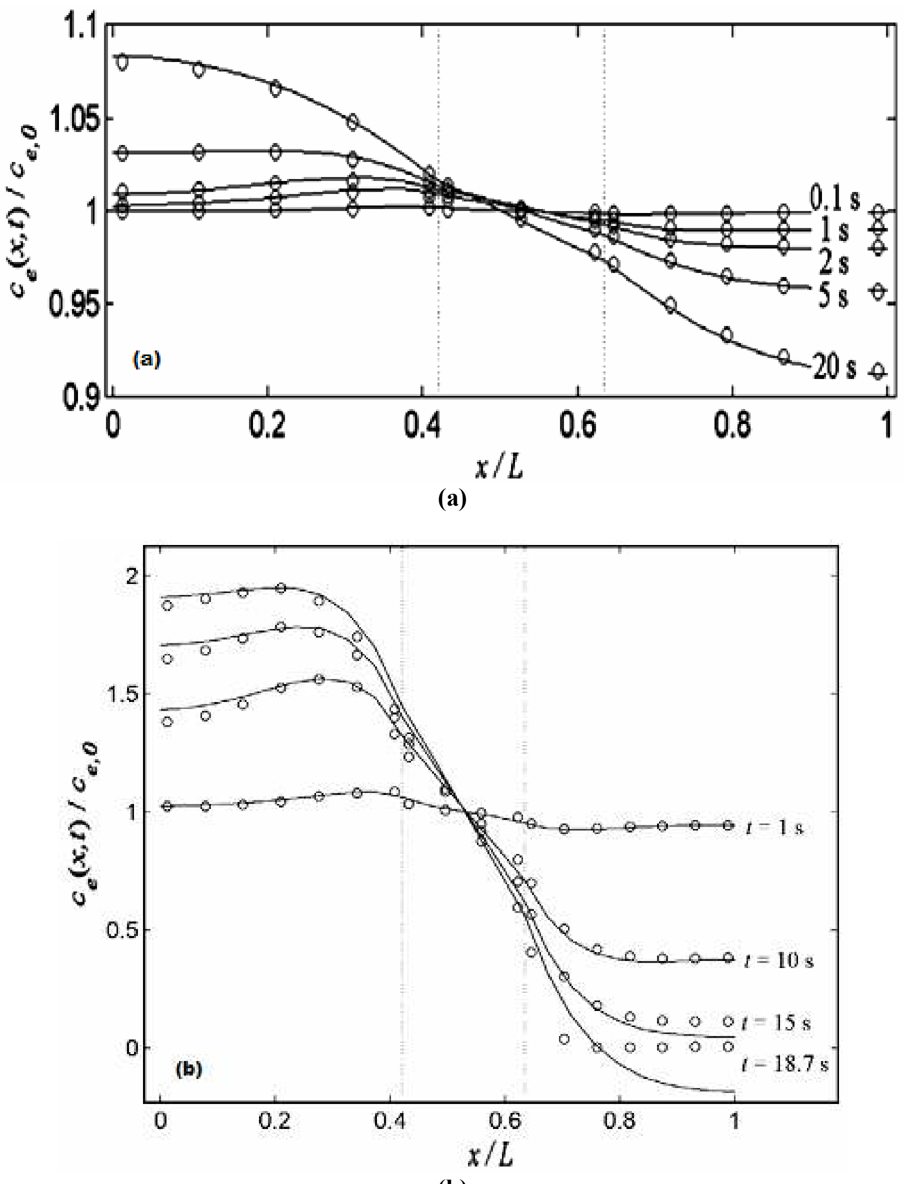


Figure 2.21: Comparison of the predictive capability of the simplified model solution by Subramanian et al. for predicting the electrolyte concentration with rigorous numerical solution. (Subramanian et al. 2007).

In Smith et al. (2007) paper, they introduced a general method to generate numerically a fully controllable state variable model from electrochemical kinetic, species and charge from partial differential equations that govern the charge and discharge behavior of a lithium-ion battery. They discussed about

- open circuit potential
- electrode surface concentration and reaction distribution coupling
- electrolyte concentration and ionic conductivity nonlinearities

According to them, these parameters are explicitly approximated in the model output equation on a local, electrode-averaged and distributed basis, respectively. They found that the balanced realization controllability and observability gramian indicates that the fast electrode surface concentration dynamics are more observable and controllable than the electrode bulk concentration dynamics. The electrolyte concentration distributions from their studies are shown in figure 2.22.



(a)

(b)

Figure 2.22: (a) Electrolyte concentration distributions during 5 C discharge from 50% SOC initial condition: CFD model (o) and 5th order negative electrode/5th order positive electrode/3rd order electrolyte linear submodels (–) and (b) Distribution of electrolyte surface concentration at various times during 30 C discharge from 100% SOC initial condition with sluggish electrolyte diffusion, $D_e = 2.6 \times 10^7$ cm^2/s. (Smith et al. 2007).

In 2009, Subramanian et al. (2009) presented an effective first step in the mathematical reformulation of physics-based lithium-ion battery models to improve computational efficiency. This was a continuation research of their previous study (Subramanian et al 2007). This study discussed more on mathematical aspect involving simplification of lithium-ion battery models such as mathematical analysis for efficient model reformulation (step-by-step mathematical detail in reducing the coupled nonlinear multiple partial differential equation from rigorous battery modeling to differential algebraic equation).

Golmon et al. (2009) presented a multi-scale finite element approach for lithium batteries in their study of electrochemical–mechanical interaction phenomena at macro-scale and micro-scale. The goal of their study is to gain understanding and quantifying the effects of electrochemical and mechanical parameters on performance and eventually, on failure mechanisms in the batteries. Hence, to achieve this goal, they developed a numerical model to predict the electrochemical–mechanical interactions in structurally integrated lithium batteries subjected to external mechanical loads. They treated the macro-scale and micro-scale models by discretized it in time using an implicit Euler backward scheme and in space using Galerkin finite element method. The nonlinear macro-scale and micro-scale subproblems are solved by Newton's method using analytically derived Jacobians. The battery model used in their paper consisted of lithium foil anode//separator//porous cathode that included solid active materials and liquid electrolyte. Then, they developed a multi-scale approach to analyze the surface kinetics and electrochemical–mechanical phenomena within a single spherical particle of the active material. They also introduced a meso-scale aggregated model to relate micro-scale and macro-scale mechanical effects. The homogenization techniques relate parameters in the micro-scale particle model (solid-phase diffusion model) to those in the macro-scale model (solution-phase diffusion model) describing the lithium-ion transport, electric potentials and mechanical response based on porous electrode theory. Several figures and graphs from Golmon et al. (2009) work are illustrated in figure 2.23 to figure 2.25.

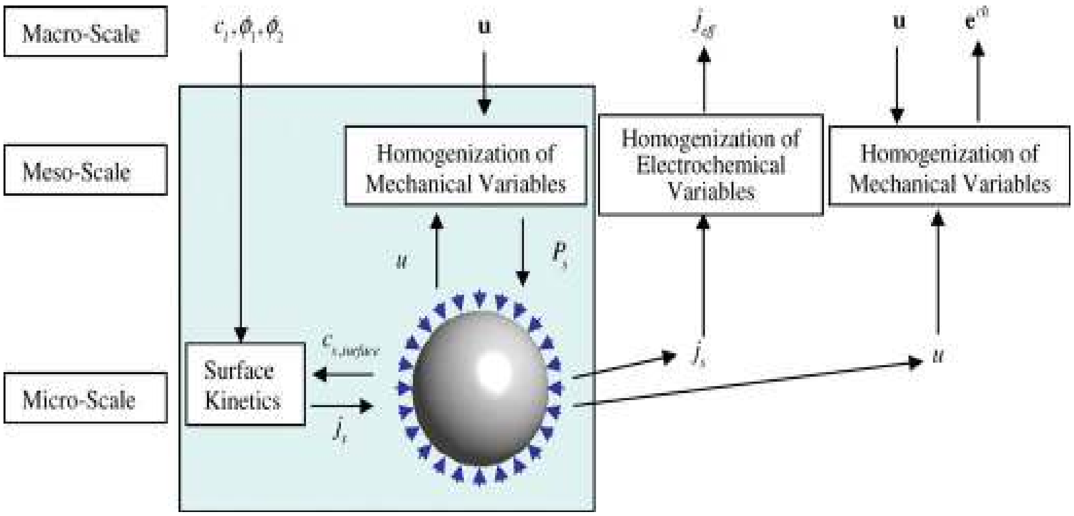
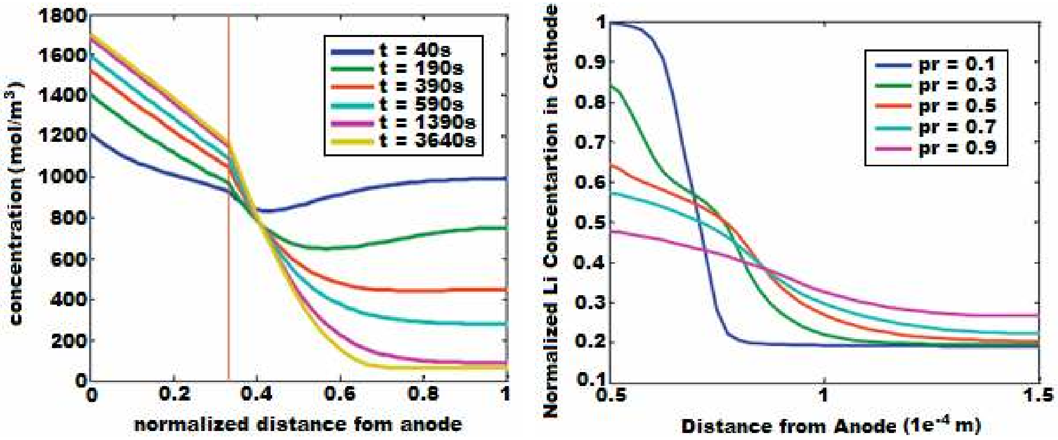
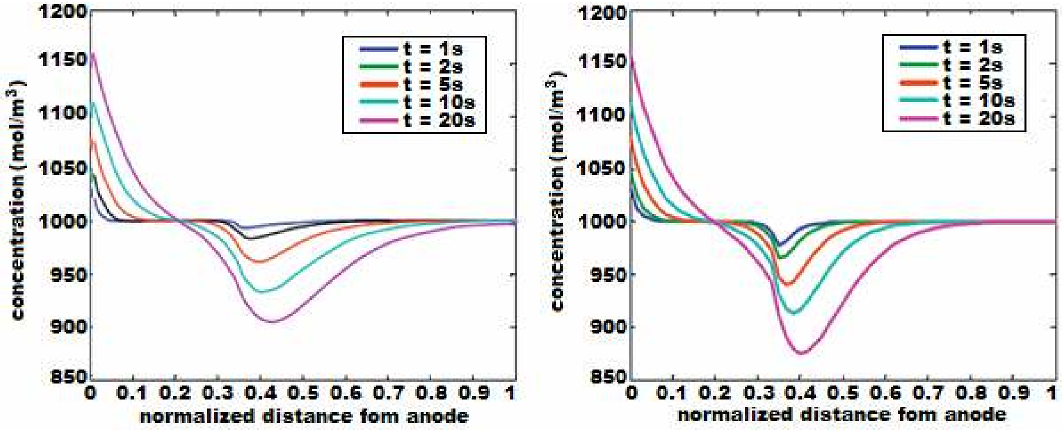


Figure 2.23: Interdependency of macro- and micro-scales. (Golmon et al. 2009).



(a) **(b)**

Figure 2.24: (a) Evolution of Li$^+$ concentration in electrolyte over time and (b) Normalized Li concentration in cathode for different porosities at average utilization of the cathode material of 0.35. (Golmon et al. 2009).



(a) **(b)**

Figure 2.25: Evolution of Li$^+$ concentration in electrolyte for $t \le 20\,s$; left: results of (Doyle et al. 1993) right: results predicted by numerical framework presented in their paper (Golmon et al. 2009).

Concurrently, the group of Abe et al. (2009) studied on high-energy-capacity battery, lithium-ion battery and high power lithium-ion battery. The purpose of their study is for application to electric vehicles (EVs), series hybrid electric vehicles (SHEVs), parallel hybrids (PHEVs). They discussed some of the battery compatibility problems for EVs, SHEVs and PHEVs. A battery simulation program was constructed to demonstrate the parameters influencing continuous power output, effect of current distribution in electrodes, effect of lithium-ion diffusion in electrode active materials and effect of lithium-ion diffusion in the electrolyte. They discovered that the electrode thickness, lithium-ion diffusion in the active materials and lithium-ion diffusion in the electrolyte are the major parameters influencing the long-duration power output characteristic. Figure 2.26 shows the simulation of lithium-ion concentration distribution in electrolyte according to Abe et al. (2009).

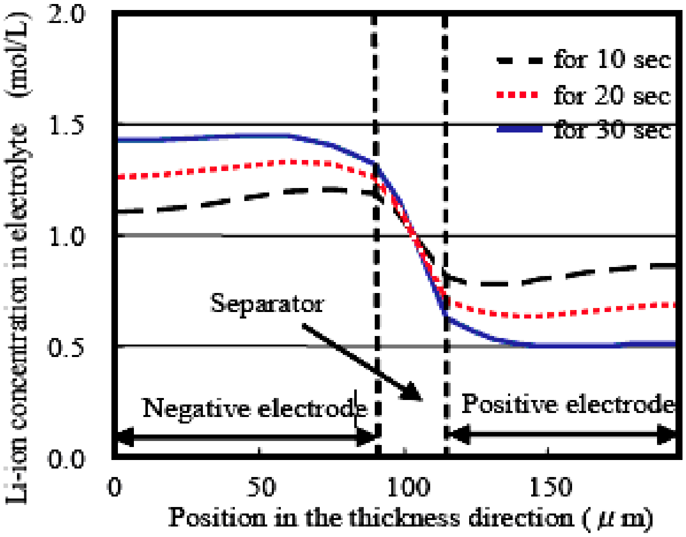
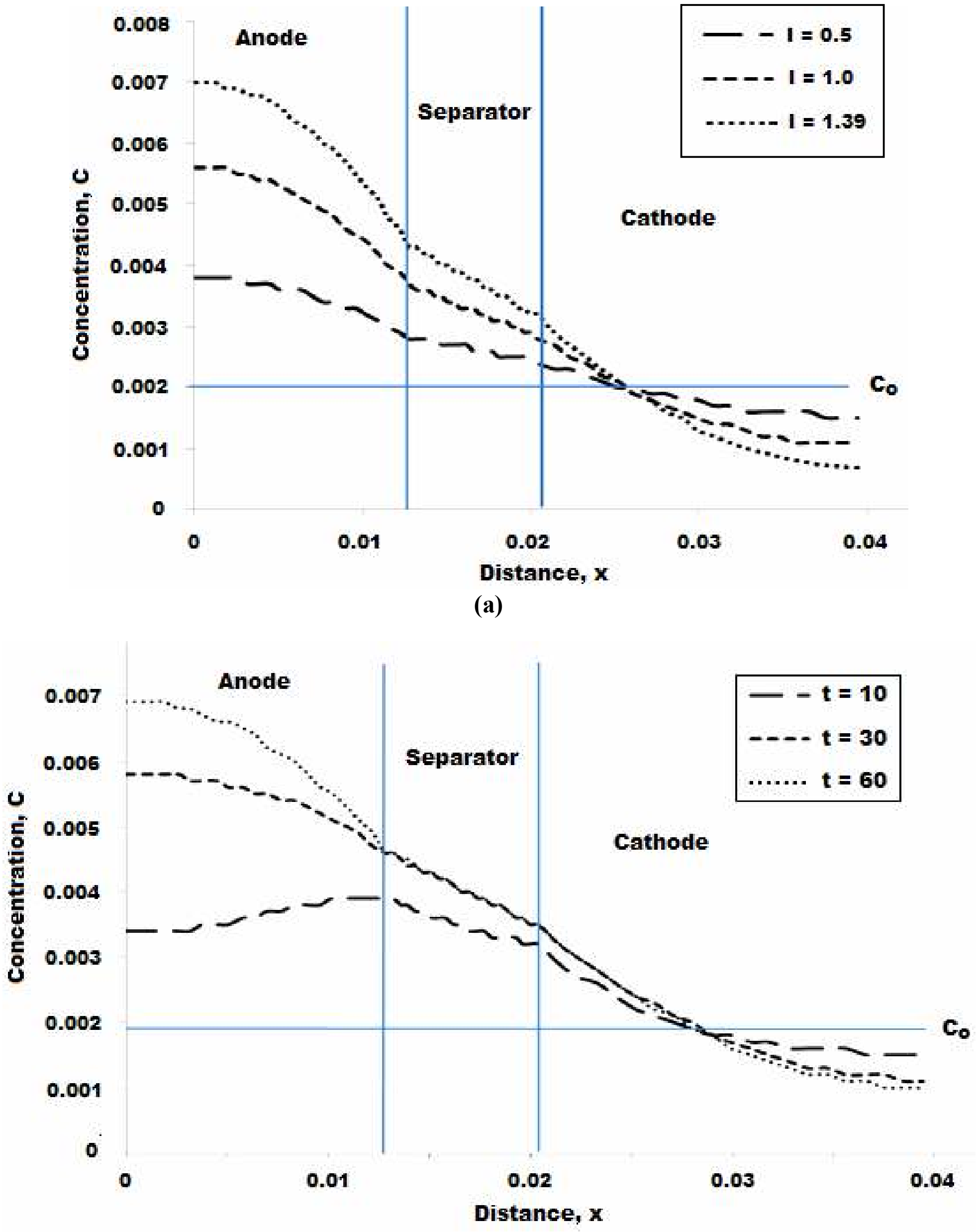


Figure 2.26: Lithium-ion concentration distribution in electrolyte. (Abe et al. 2009).

In 2010, Norzihani et al. (2010) simulated the lithium-ion concentration in solution phase for LiC_6//separator//$LiMn_2O_4$ battery system. They used FDM to solved the mathematical model which has a set of governing equations and a set of boundary conditions for anode, separator and cathode. Figure 2.27 shows their simulations' result.



(a)

(b)

Figure 2.27: Concentration profile of the lithium-ion across distance (a) at *t =30 minutes* with *I = 0.5, 1.0* and *0.5mA/cm^2* and (b) with *t = 10, 30* and *60 minutes* for *I= 1.39 mA/cm^2*. (Norzihani et al. 2010).

In 2011, Safaria and Delacourt (2011) developed a simple mathematical model for lithium intercalation and deintercalation in a lithium iron phosphate ($LiFePO_4$) electrode based on the resistive-reactant concept. This simple mathematical model was solved using Crank–Nicholson implicit method and FSOLVE subroutine embedded in MATLAB software. In order to demonstrate the importance of the resistive-reactant feature of $LiFePO_4$ electrode, 3 coin cells setup has been fabricated (cell 1 – no extra current collector, cell 2 – one extra current collector and cell 3 – two extra current collectors). Then they revealed electrochemical rate-capability analysis from these three cells, the effectiveness of the resistive-reactant concept for a quantitative description of the charge and discharge as well as the path dependence observed in lithium iron phosphate electrodes by model-experiment comparisons. Furthermore, by experiment-model analysis they made the summarization for an in-depth analysis of the path-dependence feature in the $LiFePO_4$ electrode.

The work on modeling of lithium-ion battery has progressed considerably over the last decade and will continue to improve, providing better understanding to battery researchers. It is the aim of this research to contribute a better solution to the model equations.

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